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AUSTRALIA

PATENTS ACT 1990

PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:-

"ADDITIVE FOR DEWATERABLE SLURRY"

The invention is described in the following statement:-

Technical Field

The present invention relates to admixtures for slurries and in particular cementitious slurry compositions.

Background Art

5 As is well known in the art, most cementitious compositions are laid down or used in a slurry form. Increasing difficulty and expense in obtaining high quality aggregate for use in such cementitious material such as concrete has forced manufacturers to resort to low grade materials such as crushed stone, marine sand and even recycled crushed concrete obtained from demolitions or old structures. This leads to problems with the
10 concrete such as a higher water demand, bleeding (where, as the slurry settles, water migrates to the surface), lower workability and pumpability.

In the past, these problems have been overcome by the addition of certain additives to the cementitious composition. These plasticisers, sometimes known as water reducers, dispersion agents or super plasticisers, act to increase the workability and
15 validity of the slurry for a given quantity of water. Examples include lignosulphonates, naphthalene sulphonate-formaldehyde condensates.

Typically, these water reducers are added at around 0.3% by weight of cement and provide between 8 and 12% reduction in the water cement ratio, depending upon the addition procedure. Additions of up to 1% by cement provide up to 35% reduction in the
20 water to cement ratio. In high performance concrete application, eg ultra high strength concrete, it is common to overdose in plasticiser/water reducer, (or combinations thereof) to obtain further water reduction of up to 50%. However, at such dosage levels detrimental effects are produced, eg setting times increased and compressive strength of a cementitious mixture reduced.

It is an object of the present invention to overcome or ameliorate at least one of the disadvantages of the prior art, or to provide a useful alternative.

Disclosure of the Invention

In a broad aspect, the present invention provides an additive for a cementitious
5 slurry comprising one or both of the following mineral components

- i) fly ash having a predominant particle size of less than 10 microns, and
- ii) alumina containing material having a predominant particle size less than
150 microns.

The applicants have found that use of the small particle size fraction fly ash or
10 large particle size fraction alumina containing material acts as an efficient water reducer
for cementitious slurries. The applicants have found that addition of a suitable quantity
of such a mineral additive indeed provides a substantial reduction in water required to
maintain a predetermined viscosity without any of the aforementioned detrimental
effects arising from conventional techniques. The aforementioned additive does not
15 significantly increase set times or cause excessive aeration, which can be a major
problem with some known admixtures. Further, it inhibits bleeding and improves
workability.

In a preferred embodiment, the aforementioned mineral additive can be used in
combination with a conventional water reducer/plasticiser to enhance the water reduction
20 capabilities of such a conventional additive.

In a second aspect, the present invention provides a cementitious slurry comprising
an hydraulic binder, water, and a plasticiser, and a mineral additive including one or both
of the following

- i) fly ash having a predominant particle size of less than 10 microns, and

ii) alumina containing material having a predominant particle size less than 150 microns,

the mineral additive being added in a quantity sufficient to provide a water reduction effect.

5 The reference to water reduction effect relates to the ability of the mineral additive to effectively reduce the quantity of water required to obtain a particular viscosity. As will be clear to persons skilled in the art, for certain applications, a slurry is designed to have a particular predetermined viscosity for flowability, pumpability or application reasons. The mineral additive described above provides excellent water reduction
10 properties for a slurry. As discussed, it can be used on its own to provide water reduction to the slurry or in combination with a conventional plasticiser/water reducer.

When used in combination with an amount of conventional plasticiser/water reducer, it has been found that the aforementioned mineral additive enhances the water reduction properties of the slurry as will be discussed below.

15 The fly ash in the mineral additive refers to fly ash with a predominant particle size of up to 10 microns. As will be clear to persons skilled in the art, fly ash is a solid powder having a chemical composition similar to or the same as the composition of material that is produced during the combustion of powdered coal. The composition typically comprises 25 to 60% silica, 10 to 30% Al_2O_3 , 5 to 25% Fe_2O_3 , up to about 20%
20 CaO and up to about 5% MgO.

Fly ash particles are typically spherical and range in diameter from 1 to 100 microns. It is the smaller size fraction of fly ash particles with a predominant size below 10 microns that has surprising water reduction properties.

The fly ash preferably makes up 30-100% based on weight of cement. Preferably, the fly ash is between 40 and 90% and most preferably 50 to 70% based on weight of cement.

Larger size fly ash particles have been known in the past to provide a water reduction effect. Smaller size particles, however, have always been considered unsuitable for water reduction for a few reasons. Firstly, it is expected in the art that the smaller the particle size, the more reactive the particle. Fly ash is a reactive pozzolan and accordingly, smaller size fraction fly ash was considered inappropriately reactive to act as a water reducer.

In addition, due to the high specific surface area of the smaller size fraction fly ash, it was expected that this material would in fact increase water demand. The applicants have surprisingly found that the opposite is in fact the case. The smaller size fraction fly ash boosts the water reducing properties of conventional water reduction agents by a substantial extent.

The alumina in the mineral additive has a predominant particle size less than 150 microns. The reference to alumina should not be taken literally but refers to alumina type materials including hydrated and unhydrated alumina. Preferably, the alumina content based on the weight of cement is between 5 and 30%, preferably 10 to 25% and most preferably 15 to 20%.

If a blend of hydrated alumina and fly ash is used in the mineral additive, the ratio of hydrated alumina:fly ash is between 1:1 to 1:10.

The term "hydraulic or cementitious binder" as used herein, means all inorganic materials which comprise compounds of calcium, aluminium, silicon, oxygen, and/or sulfur which exhibit "hydraulic activity" that is, which set solid and harden in the

presence of water. Cements of this type include common Portland cements, fast setting or extra fast setting, sulphate resisting cements, modified cements, alumina cements, high alumina cements, calcium aluminate cements and cements which contain secondary components such as fly ash, slag and the like. The amount of cement present in the
5 composition of the present invention has a lower limit of 10 weight percent based on the total dry ingredients, preferably 15 weight percent, more preferably 20 weight percent, the upper limit of the amount of the cement is 50 weight percent, preferably 40 weight percent, more preferably 30 weight percent.

The cementitious composition may optionally but preferably include at least one
10 filler material, e.g. graded and ungraded aggregate such as washed river gravel, crushed igneous rock or limestone, lightweight aggregate, crushed hard-burnt clay bricks or air-cooled blast furnace slag, sand, calcium carbonate, silica flour, vermiculite, perlite, gypsum .. etc.

The amount of filler present in the cementitious composition has a lower limit of 5
15 weight percent based on the total dry ingredients, preferably 10 weight percent, more preferably 15 weight percent; the upper limit being 30 weight percent, preferably 25 weight percent, more preferably 20 weight percent.

The cementitious composition may optionally contain other additives including:
cement plasticising agents such as melamine sulphonate-formaldehyde
20 condensates, naphthalene sulphonate-formaldehyde condensates, naphthalene sulphonates, calcium lignosulphonates, sodium lignosulphonates, saccharose, sodium gluconate, sulphonic acids, carbohydrates, amino carboxylic acids, polyhydroxy carboxylic acids, sulphonated melamine, and the like.

The amount of conventional plasticiser used in the dry cement composition will vary, depending on the fluidising ability of the particular cement plasticiser selected. Generally, the amount of cement plasticiser is preferably in the range of about 0.3 to about 3 wt %, and more preferably about 0.5 to about 2 wt %, based on the weight of the dry cement composition.

Preferred plasticisers include Melment. F-10, a melamine-formaldehyde-sodium bisulphite polymer dispersant, marketed by SKW-Trostberg in the form of a fine white powder. Another suitable plasticiser is Neosyn, a condensed sodium salt of sulphonated naphthalene formaldehyde, available from Hodgson Chemicals.

Thickener may also be used in the cementitious composition including one or more of the polysaccharide rheology modifiers which can be further subdivided into cellulose based materials and derivatives thereof, starch based materials and derivatives thereof, and other polysaccharides.

Suitable cellulose based rheology-modifying agents include, for example, methylhydroxyethylcellulose, hydroxymethylethylcellulose, carboxymethylcellulose, methylcellulose, ethylcellulose, hydroxyethylcellulose, hydroxyethylpropylcellulose, etc. The entire range of suitable rheology modifiers will not be listed here, nevertheless, many other cellulose materials have the same or similar properties as these and are equivalent.

Suitable starch based materials include, for example, amylopectin, amylose, sea-gel, starch acetates, starch hydroxyethyl ethers, ionic starches, long-chain alkylstarches, dextrans, amine starches, phosphate starches, and dialdehyde starches.

Other natural polysaccharide based rheology-modifying agents include, for example, alginic acid, phycocolloids, agar, gum arabic, guar gum, welan gum, locust bean gum, gum karaya, and gum tragacanth.

The thickener addition rate in the cementitious composition may range between
5 0.0001 and 0.5 % based on the weight of the dry cement composition.

Latex addition of at least one latex selected from the group consisting of: an acrylic latex, a styrene latex, and a butadiene latex is also preferred. This component improves adherence, elasticity, stability and impermeability of the cementitious compositions containing it, and also favours formation of flexible films.

10 The latex may be used in solid amounts of about 0.5 to about 20 wt %, based on the weight of the dry cement composition. Preferably, it is present in an amount of about 1 to about 15 wt %, and more preferably about 10 wt %, based on the weight of the dry cement composition.

The cementitious composition may optionally incorporate as a substitute to the
15 latex emulsion a proportion of a powdered vinyl polymer or other equivalent polymeric material, to enhance the adhesion; resilience and flexural strength; and abrasion resistance of the composition.

The powdered vinyl polymer is preferably polyvinyl acetate or a copolymer of vinyl acetate with another monomer, such as ethylene. A preferred vinyl acetate resin is
20 VINNAPAS LL5044 thermoplastic resin powder, containing a vinyl acetate-ethylene copolymer, available from WACKER.

The powdered vinyl polymer may be used in amounts of about 0.5 to about 20 wt %, based on the weight of the dry cement composition. Preferably, it is present in an amount of about 1 to about 15 wt %, and more preferably about 10 wt %, based on the

weight of the dry cement composition.

The cementitious composition may optionally contain 0-40 wt % of other fillers/additives such as mineral oxides, hydroxides and clays, metal oxides and hydroxides, fire retardants such as magnesite, thickeners, silica fume or amorphous silica, colorants, pigments, water sealing agents, water reducing agents, setting rate modifiers, hardeners, filtering aids, plasticisers, dispersants, foaming agents or flocculating agents, water-proofing agents, density modifiers or other processing aids

Mode(s) for Carrying out the Invention

So that the present invention may be more clearly understood it will now be described by way of example only with reference to the following embodiments.

Example 1: Effect of water reducer and small size fraction fly ash addition on % water reduction in a cement: fly ash mixture

Three mixes (total weight of solids = 1000 gm each) were mixed with water to achieve a mix viscosity of 4 - 3 seconds cup drainage time. The details of the mixes are shown in Table 1 below.

Table 1

Mix ingredients	Mix 1 weight, gm	Mix 2 weight, gm	Mix 3 weight, gm
Cement	300 gm	300 gm	300gm
Fly ash (large size fraction)	700 gm	700 gm	500 gm
Fly ash (small size fraction)	-	-	200 gm
Water reducer (sulphonated naphthalene formaldehyde)	-	3 gm	3 gm
Styrene Acrylic Latex Emulsion (56% solids)	60 ml	60 ml	60 ml
Welan Gum (Kelcocrete)	0.1 gm	0.1 gm	0.1 gm
Water	550ml	350 ml	325 ml
Water reduction in mix, %	-	36%	41%
Viscosity (drainage time in 50 ml cup)	3 seconds	3 seconds	4 seconds

It can be seen that the addition of 1% water reducer by weight in cement resulted in 36% reduction in mix water. This level of water reduction is, according to literature, about the limit of what can be achieved at such high water reducer dose. Using higher
5 doses would result in excessively delayed setting time and reduction in the compressive strength in cementitious mixes. When part of the large size fraction fly ash was substituted with smaller size fraction (predominant particle size less than 10 microns) in mix 3, further water reduction was achieved, bringing total water reduction to 41%. This result is quite surprising, as the finer fly ash was expected to in fact increase the water
10 demand in the mix due to its high surface area.

Although the water reducing effect of fly ash in cementitious mixes is well documented in literature, the plasticity enhancing effect of the smaller size fraction in an already plasticised cement:fly ash mixture is considered surprising given the universal rule that finer material exhibit larger surface area, leading to an increase in the water
15 demand, needed as mechanical water coating the finer particles.

Example 1 demonstrates a means of enhancing the water reduction effect in plasticised mixes using a mineral additive with a specified size range, namely the small size fraction fly ash, without resorting to overdosing with water reducer. The result is a more durable mix with higher strength and reduced shrinkage.

20 Example 2: Water reduction in plasticised mixes substituting large size fraction fly ash for smaller size fraction fly ash

Two mixes (total weight of solids = 1000 gm each) were mixed with water to achieve a mix viscosity in the range of 6 – 10 Poise. The details of the two mixes are shown in Table 2 below.

Table 2

Mix ingredients	Mix 1 weight, gm	Mix 2 weight, gm
Cement	300 gm	300 gm
Fly ash (large size fraction)	400 gm	250 gm
Fly ash (small size fraction)	-	150 gm
Cenospheres	300 gm	300 gm
Melment 15 (SKW Chemicals) (sulphonated melamine formaldehyde)	3 gm	3 gm
MC 1834 Acrylic Resin (Rohm & Haas)	10 ml	10 ml
Water	400 ml	325 ml
Water reduction	-	19%
Viscosity (Rotothinner)	6.5 Poise	8.8 Poise

It can be seen that Mix 1 which was comprised of cement, fly ash and cenospheres (ceramic hollow spheres) required 400 ml of water to achieve the required viscosity (in the presence of 1% addition of Melment F15 water reducer). The % solids in this case is 71.4%.

Mix 2, however, required only 325 ml of water to achieve a similar flowability. Such water reduction (around 20%) was enabled by substituting part of the larger fly ash particles with a smaller size fraction (minus 10 microns in size, average size = 4 microns). The % solids in this case was increased to 75.5%.

Example 3: Water reduction in plasticised mixes comparison of silica to fly ash.

Two mixes (total weight of solids = 1000 gm) were mixed with water to achieve a mix viscosity of 4 - 3 seconds cup drainage time. The details of the two mixes are shown in Table 3 below.

Table 3

Mix ingredients	Mix 1 weight, gm	Mix 2 weight, gm
Cement	300 gm	300gm
Fly ash (large size fraction)	500 gm	500 gm
Fly ash (small size fraction)	-	200 gm
Silica	200 gm	-
Water reducer (sulphonated naphthalene formaldehyde)	3 gm	3 gm
Styrene Acrylic Latex Emulsion (56% solids)	60 ml	60 ml
Welan Gum (Kelcocrete)	0.1 gm	0.1 gm
Water	400 ml	325 ml
Water reduction in plasticised mix	-	19%
Viscosity (drainage time in 50 ml cup)	4 seconds	4 seconds

It can be seen that Mix 1 which was comprised of cement, fly ash and silica required 400 ml of water to achieve the required viscosity (in the presence of 1% water reducer addition). The % solids in this case is 71.4%.

Mix 2, however, required only 325 ml of water to achieve a similar flowability. Such water reduction (around 20%) was enabled by substituting the silica with ultra fine fraction (minus 10 microns in size, average size = 4 microns). The % solids in this case was increased to 75.5%.

10 Example 4: Water reduction in plasticised mixes incorporating combination of hydrated alumina and fly ash

In Table 4, the water requirements for two mixes containing 1.0 % addition (by weight of cement) of a water reducer, ie sulphonated naphthalene formaldehyde, are compared.

Table 4

Mix ingredients	Weight (Mix 1) without hydrated alumina	Weight (Mix 2) With hydrated alumina
Cement	10000 gm	10000 gm
Fly ash (large size fraction)	16000 gm	16000 gm
Fly ash (small size fraction)	8000 gm	8000 gm
Calcium Carbonate (Omyacarb Grade 40)	6000 gm	4000 gm
Hydrated Alumina	-	2000 gm
Water reducer (naphthalene formaldehyde sulphonate)	100 gm	100 gm
Welan Gum (Kelcocrete)	3 gm	3 gm
Styrene Acrylic Latex Emulsion (56% solids)	2000 ml	2000 ml
Water	16500 ml	12500
Water reduction in plasticised mix, %	-	25%
Viscosity (drainage time in 50 ml cup)	3.5 seconds	3 seconds

It can be seen that the addition of 2000 gm of hydrated alumina in mix 2 (in substitution of calcium carbonate), resulted in a significant reduction in the water demand, ie from 16500 to 12500 ml, for the same viscosity level.

This level of water reduction (around 25% in an already heavily plasticised mix) is quite unexpected. It is also contrary to conventional water reduction trends presented in cement chemistry literature which suggest that the amount of water reduction ranges generally between 15% to 35%, and that (beyond a particular dosage) further water reduction is not possible (Concrete Admixtures Handbook by, Ramachandran, 2nd edition, page 447).

From the examples outlined above it can be seen that using a mineral additive comprising small size fraction fly ash and/or alumina containing materials provide water reduction in non-plasticised cementitious mixes or additional/enhanced water reduction in plasticised cementitious mixes containing a conventional water reducing agent. Such

high performance cementitious mixes (lower shrinkage, higher strength, more durable), without the disadvantages of overdosing with conventional organic water reducers, ie delayed setting time, strength reduction, excessive aeration . etc.

It will be understood that the modifications or variations can be made to the
5 aforementioned embodiments without departing from the spirit or scope of the present
invention.

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